COPPER AND IRON INCORPORATED MCM-41 FOR THE HETEROGENEOUS OXIDATION OF BENZYL ALCOHOL

by

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LIST OF SYMBOLS AND ABBREVIATIONS

AAS	Atomic absorption spectroscopy
BET	Brunaure, Emmett, Halenda
CTAB	Cetylmethylammonium bromide
Cu-5	Copper incorporated MCM-41 with 5 % metal loading
Cu-10	Copper incorporated MCM-41 with 10 % metal loading
Cu-15	Copper incorporated MCM-41 with 15 % metal loading
Cu-20	Copper incorporated MCM-41 with 20 % metal loading
DMSO	Dimethyl sulfoxide
E_a	Activation energy
EDX	Energy dispersive X-ray spectroscopy
Fe-5	Iron incorporated MCM-41 with 5 % metal loading
Fe-10	Iron incorporated MCM-41 with 10 % metal loading
Fe-15	Iron incorporated MCM-41 with 15 % metal loading
Fe-20	Iron incorporated MCM-41 with 20 % metal loading
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometer
IUPAC	The International Union of Pure and Applied Chemistry
RH	Rice husk
RHA	Rice husk ash
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TEOS	Tetra ethyl orthosilicate

XRD	Powder X-ray diffractometry

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KUPRUM DAN FERUM DIGABUNGKAN DALAM MCM-41 UNTUK PENGOKSIDAAN HETEROGEN BENZIL ALKOHOL

ABSTRAK

MCM-41 yang digabungkan dengan 10 % kuprum dan ferum dihasilkan melalui teknik sol-gel pada suhu bilik. Pemangkin yang dihasilkan dilabel sebagai Cu-10 dan Fe-10. Abu sekam padi digunakan sebagai sumber silika. Dalam kajian ini, pemangkin-pemangkin tersebut dicirikan dengan menggunakan FTIR, XRD, analisis penyerapan nitrogen, TEM, SEM dan ujian penyerapan piridina. Daripada analisis pencirian, hasil menunjukkan rangka MCM-41 masih kekal bergantung kepada peratus kemasukan kuprum dan ferum. Selain itu, hasil analisis menunjukkan bahan MCM-41 dengan susunan liang heksagon boleh dihasilkan di dalam suhu bilik dengan kehadiran kuprum dan ferum. Mangkin Cu-10 dan Fe-10 telah diuji dalam pengoksidaan benzil alkohol dengan hidrogen peroksida sebagai pengoksida. Ferum digabungkan dalam MCM-41 memberikan aktiviti pemangkin yang tinggi berbanding dengan mangkin lain dengan 67 % penukaran benzil alkohol dan 85 % selektiviti terhadap benzaldehid.

COPPER AND IRON INCORPORATED MCM-41 FOR THE HETEROGENEOUS OXIDATION OF BENZYL ALCOHOL

ABSTRACT

MCM-41 incorporated with 10 % copper and iron was synthesized via sol—gel technique at room temperature. The catalysts were labelled as Cu-10 and Fe-10 respectively. Rice husk ash (RHA) was used as the silica source. In this research, the catalysts were characterized by using FTIR, XRD, Nitrogen sorption analysis, TEM, SEM and pyridine adsorption test. From the characterization analysis, the results showed that the MCM-41 framework was maintained depending on the percentage loading of copper and iron. In addition, the results indicated that MCM-41 materials with a hexagonal array of uni-directional pores could be synthesized successfully at room temperature in the presence of copper and iron. Cu-10 and Fe-10 catalysts have been tested in the oxidation of benzyl alcohol with hydrogen peroxide as oxidant. Iron incorporated MCM-41 gives higher catalytic activity compared to other catalyst with 67 % conversion of benzyl alcohol and 85 % selectivity to benzaldehyde.

CHAPTER 1

INTRODUCTION

1.1 Background

Catalyst increases the rate of a reaction (Erhard, 1989). There are two types of catalyst, homogeneous and heterogeneous catalysts. Homogeneous catalyst is where the catalyst and reactant are in the same phase while heterogeneous catalyst is where the catalyst and reactant are in different phases. Nowadays, heterogeneous catalysts are widely used in chemical reactions due to its ease of separation and environmental friendly properties.

1.2 Oxidation catalysis

Heterogeneous catalysts are used as catalysts for selective oxidation of hydrocarbons within the fine chemical industry (Sheldon, et al., 2004). The selective oxidation of hydrocarbon is important due to its valuable products such as aldehyde, ketone and epoxide. Sometimes, the catalyst used in the oxidation process will help to control the selectivity to prevent over oxidation that will lead to carboxylic acid as the products.

Iron and copper are among transition metals that have been widely used in the alkane, alkene and alcohol oxidation. Transition metal consists of partially filled *d*-orbitals. Thus, electron transfers from the reactants to these partially empty d-orbitals on the surface of these transition metals are believed to take place during catalytic activity (Clark, 1953).

Iron with the ground state electronic configuration [Ar] $3d^6\ 4s^2$ is known to have several oxidation states from −2 to + 6, although +2 and +3 are the most common. It is a transition element that is located in group 8 period 4 in the periodic

table. It is a lustrous metal with a grayish tinge. Iron chemical compounds, which include ferrous and ferric compounds, have many uses. Iron metal is quite cheap. Iron plays an important role in biology as it is used as the active site for many important redox enzymes, which deals with cellular respiration, oxidation and reduction in plants and animals. In addition, iron incorporated onto silica support has successfully acted as an oxidation catalyst for various oxidation process (Adam, et al., 2006).

Copper metal is located in group 11 period 4 in the periodic table. The electronic configuration is [Ar] $3d^{10}$ $4s^{1}$. It is a ductile metal with very high thermal and electrical conductivity. Copper compounds are known to exist in several oxidation states, where usually it exists in the oxidation state of +2. Copper can act as a catalyst. For example, it speeds up the reaction between zinc and dilute sulphuric acid. The heterogeneous catalyst using copper incorporated with support has been used in oxidation and epoxidation reactions (Hamza, et al., 2009).

Even though homogeneous catalysts give higher product conversion and selectivity, it is still not favored in fine chemical industry due to several factors. Cornils and Herrmann, (2003) stated that, the ratio between heterogeneous and homogeneous catalysts used in the industry is 75:25.

Homogeneous catalysts are often associated with some disadvantages such as toxicity, corrosion and difficulty in recover as the separation of the reaction mixture is difficult (Sheldon, et al., 2000). It is known as a non-environmentally friendly catalyst. Thus, heterogeneous catalysts are widely used to overcome the disadvantages of homogeneous catalysts. Heterogeneous catalysts have good thermal stability with ease of catalyst recovery. This makes heterogeneous catalyst much more favored in fine chemical industry.

Chemical synthesis can take place in the vapor phase and liquid phase. For the liquid phase, water is the most preferred solvent. However, if water is used as the solvent, oxidation of alcohol will form the corresponding carboxylic acid. Therefore, to avoid this from happening, dry conditions are required (Mallat and Baiker, 2004).

1.3 Rice husk ash (RHA)

Silica (SiO_2) can exist in a variety of forms with its own structural properties and chemical and physical characteristics. Silica can exist as crystalline, gel and amorphous form (Adam, et al., 2012). Silica can be found as sand, clays, soil and rocks. Silica can also be synthesized from commercial starting materials such as tetraethoxysilane (TEOS), tetrapropoxysilane (TPOS) and tetramethoxysilane (TMSO) (Paulino and Schuchardt, 2002). These chemicals are expensive and toxic (Nakashima, et al, 1998).

In order to avoid these unfavorable sources, naturally occurring, cheaper and safer silica from plants is studied. Silica from agricultural by-products such as rice husk (RH) is widely known in rice-producing countries (An, et al., 2010). RH was used as an energy source in many industries such as biomass power plant and in rice mill. Rice husk ash (RHA) rich in silica will be produced when RH is burnt. Kalapathy, et al., (2000) concluded that, RHA can be an economically valuable raw material for natural silica production.

RH is composed of 20 % ash, 38 % cellulose, 22 % lignin, 18 % pentose and 2 % other organic moieties (Adam, et al., 2006). Radhika and Sugunan, (2006), found that RH can produce silica with a purity of ca. 92-95 % and this silica can be further purified to 99 %. The images of RH and RHA are shown in Fig. 1(a) and (b).

(a)

(b)

Fig 1.1: The images of (a) RH and (b) RHA

RHA as a silica precursor has been used to synthesize mesoporous materials such as MCM-41 (Michorczyk, et al., 2008; Adam and Kueh, 2013; Appaturi and Adam, 2013), MCM-48 (Wang, et al., 2009) and SBA-15 (Wang, et al., 2009; Zhao, et al., 2010). Transition metal can be incorporated into these mesoporous materials to produce heterogeneous catalysts for various oxidation, epoxidation and dehydrogenation reactions.

1.4 Mesoporous molecular sieves MCM-41

In 1992, Mobile Crystalline Materials (MCM), a new family of molecular sieves was discovered and developed by Mobil Oil Research and Development scientists by using a templating mechanism (Hui and Chao, 2006). Mobil Catalytic Material Number 41 (MCM-41) shows a highly ordered hexagonal array of uni-directional pores with a very narrow pore size distribution (Kleitz, et al., 2001). Sakthivel, et al., (2006) stated that, the presence of silanol groups on the MCM-41 surface area is important in order to generate the active sites for potential catalytic activity. MCM-41 has been developed in order to make it more efficient and stable for applications in catalysis, separations, sorption, polymer chemistry, coatings, and chemical sensing (Vartuli, et al., 1998; Samanta, et al., 2003).

In order to achieve a defined pore diameter, surfactant plays an important role to form micelles in the synthesis solution. It will form templates that help to build the MCM-41 framework. The common surfactant used in the preparation of MCM-41 is cetyltrimethylammonium bromide (CTAB). Fig. 1.2 shows the schematic representation for the formation of MCM-41 (Gibson, 2014**)**. First, the surfactant forms rod-like micelles that align into hexagonal arrays. Silica is then later added to cover the rods. Next, calcination will lead to the condensation of the silanol groups. The condensation of the silanol groups will make the silicon atoms bridged by oxygen atoms. During the calcination, the organic template is oxidized and disappears.

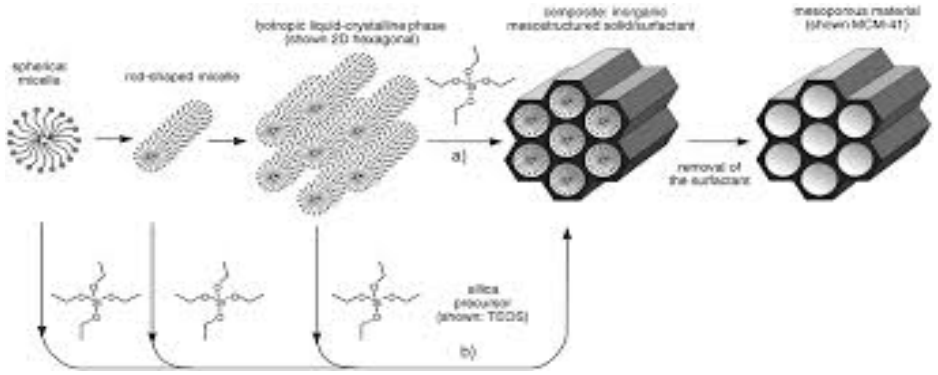


Fig. 1.2: The schematic representation for the formation of MCM-41 [Gibson, 2014].

1.4.1 MCM-41 as support catalyst

MCM-41 is a mesoporous material. Although it is composed of an amorphous silica wall, it posses long range ordered framework with uniform mesopores. This material has a large surface area, which can exceed more than 1000 m^2g^{-1}. The size of mesopores range between 2 and 50 nm (Corma, 1997). The large pore size and ordered pore morphology allow reactant molecules that are small enough to diffuse into the pores. However, the use of pure silica materials as catalysts is limited by their lack of sufficient acidity and redox properties. But, the

incorporation of heteroatoms into the silicate framework could change their surface properties and improve the catalytic activity.

The hexagonal MCM-41 has attracted much research attention because of its potential applications as catalyst supports and adsorbent. It shows good catalytic activity as well as good thermal and hydrothermal stability when incorporated with metal (Burkett, et al., 1996). The MCM-41 is generally synthesized from various silica sources such as sodium silicate, fumed silica or tetraethoxysilane (TEOS) and alkali surfactant solutions (C12-C18) as its template (Kleitz, et al., 1997]. RHA can also be an alternative for the synthesis of MCM-41. The use of RH as a silica source can result in solving its disposal problems.

From the chemical modification point of view, the hydrothermal stability of MCM-41 material can be improved by enhancing the surface hydrophobicity (with organic modifiers) or increasing the pore wall thickness (with inorganic modifiers) (Zhao, et al., 2000). The modifications can be used to adjust the surface functionality, to incorporate catalytic functions or to change textural properties.

MCM-41 incorporated with metal can be used as a catalyst for various chemical reactions for the production of chemicals in the industry and as an adsorbent in waste water treatment (Kleitz, et al., 2001). For oxidation catalyst, transition metals such as iron, copper, titanium, vanadium and cobalt have been incorporated into MCM-41 (Burkett, et al., 1996). The ability of the transition metal is to undergo facile transitions between oxidation states, to coordinate to a substrate and to be a good source or sink for electrons makes transition metals such a good catalyst. Vanadium incorporated MCM-41 was used as a catalyst in the oxidation of benzene and cyclohexane (Chen and Lu, 1999). Molybdenum, chromium, vanadium

and bismuth have been incorporated with MCM-41 for use as catalysts for cyclohexane oxidation (Kana, et al., 1998; Sakthivel and Selvam, 2002; Dapurkar, et al., 2004; Qian, et al., 2005). MCM-41 has also been incorporated with both metal and organic complexes. Hamza and Srinivas (2009) studied the copper phthalocyanine immobilized on MCM-41 on the selective oxidation of benzyl alcohol.

1.4.2 Techniques of heterogenization of iron and copper

There are various methods for metal to be incorporated with silica. Each method contributes to different properties of catalysts such as the surface properties and nature of active and adsorption sites. There are two techniques that have always been compared together; the sol-gel technique and the impregnation technique.

Metal incorporated via sol-gel technique will give a different catalyst compared to the incorporation of metal via the impregnation technique (Lopez, et al., 1994). In the sol-gel technique, the metal and support interaction is stronger compared to the impregnation technique. This is due to the metal particles that are dispersed within the matrix of the support (Wang, et al., 2003). This indicates that, in the sol-gel technique the metal species would be better stabilized in the support. In the sol-gel technique, the metal and silica are mixed in the solution phase. The metal as metal ion and silica as sodium silicate are mixed together. This mixture is neutralized to form the metal-silica composite in the form of MCM-41.

Based on the BET results, catalyst synthesized via sol-gel technique has a larger surface area compared to the catalyst synthesized via impregnation technique (Wang, et al., 2003). In the sol-gel technique, metal ions are incorporated into the support. On the other hand, in the impregnation technique, the metal tends to react

with oxygen and metal oxide will be formed. The pores of the support then will be partially filled with metal oxide particles. A higher loading of metal using this method will be difficult to achieve due to pores getting clogged during the process (Cannas, et al., 2004).

Adam, et al. (2010) incorporated chromium into rice husk ash silica via sol-gel technique. The prepared catalyst gives 99.92 % conversion of styrene with 82.15 % selectivity of benzaldehyde. RHA silica functionalized with APTES (RHAC-NH_2) via sol-gel technique was synthesized by Adam and Ooi (2012). This was immobilized with [tetrakis(*o*-chlorophenyl)prophyrinato]Co(II) which acted as an excellent catalyst for the oxidation of benzyl alcohol to benzaldehyde. The conversion of benzyl alcohol was 97.1 % with 97.7 % selectivity to benzaldehyde. In addition, catalysts prepared by the sol-gel technique required less time in order to give a high conversion and selectivity.

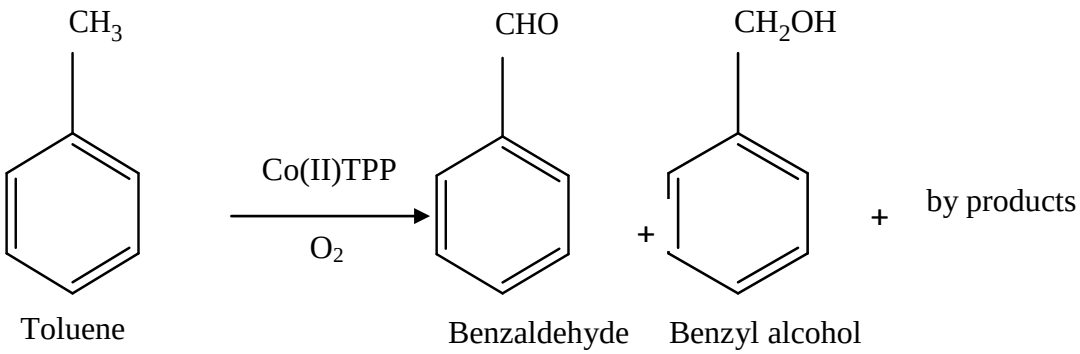
1.5 The synthesis of benzaldehyde

Benzaldehyde is an organic compound, which is a colorless liquid and has a pleasant almond-like odor. It is the simplest aromatic aldehyde (C_6H_5CHO) and acts as one of the most useful starting material and intermediate in fine chemical industry. Benzaldehyde acts as an important intermediate for the production of dyestuff, perfumery and pharmaceuticals. Other than that, benzaldehyde can be converted into the derivatives of cinnamaldehyde and styrene. Mandelic acid is an aromatic alpha hydroxyl acid which can act as a precursor to various types of drugs. It is prepared by reacting benzaldehyde with hydrocyanic acid. The resulting nitrile is then hydrolyzed to mandelic acid.

Benzaldehyde can be obtained from natural sources and chemically synthesized. Benzaldehyde can be synthesized via various processes such as oxidation of toluene, oxidation of styrene and partial oxidation of benzyl alcohol. Apple, apricot, prune, peach and cherry kernels are known to contain a significant amount of amygdalin. The reaction of amygdalin with water under enzyme catalysis yields benzaldehyde, hydrocyanic acid and two glucose molecules. The benzaldehyde from natural sources is not safe to be consumed because of the hydrocyanic acid decomposition. Hydrocyanic acid is a dangerous substance that will harm human body (Scott and Scott, 1922).

1.5.1 Oxidation of toluene

Benzaldehyde can be produced from toluene oxidation. This process can be done in a liquid-phase and vapor phase reaction. There are limitations in vapor phase reaction as the conversion is always not more than 70 % with carbon dioxide as the main by-product (Borgaonkar, et al., 1984). Cobalt tetraphenylporphyrin, Co(II)TTP, was used as a catalyst for the oxidation of toluene to benzaldehyde with molecular oxygen as the oxidant (Guo, et al., 2005). The reaction used nitrogen gas to maintain the pressure. The products obtained were benzaldehyde, benzyl alcohol and benzoic acid. The toluene conversion was 8.9 % with 33 % of benzaldehyde selectivity. Scheme 1.1 below shows the oxidation of toluene by Co(II)TTP.

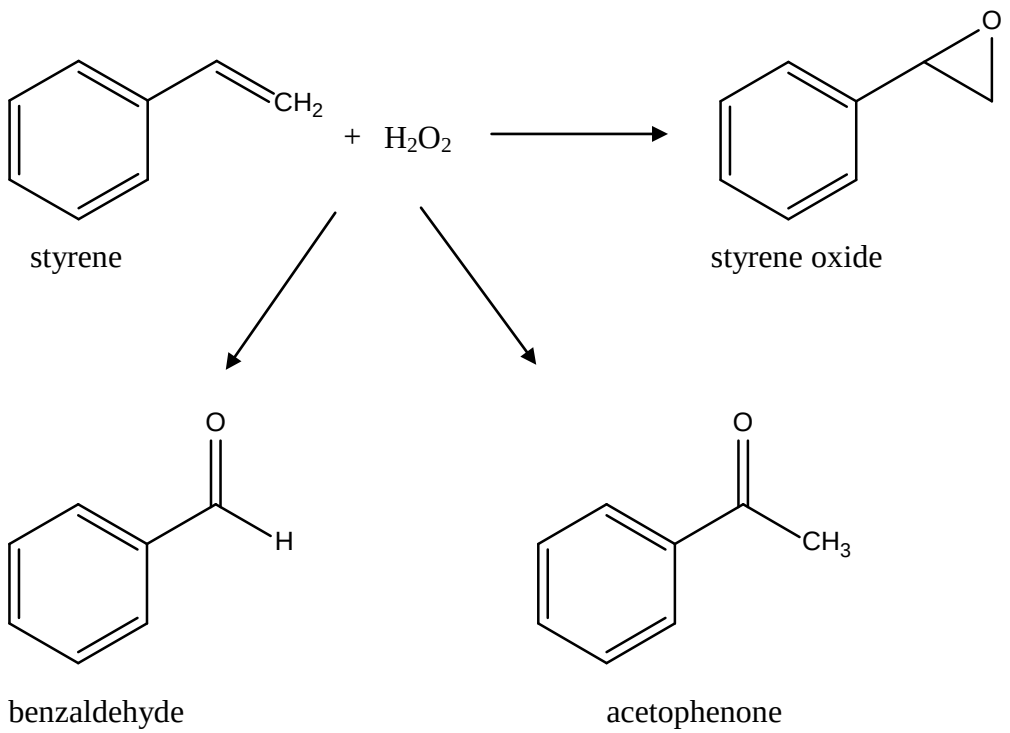


Scheme 1.1: Oxidation of toluene catalyzed by Co(II)TTP catalyst.

Li, et al., (2013) synthesized iron-modified HZSM-5 materials by the impregnation technique. The reaction was run at 90 ^{o}C for 4 hours. The toluene conversion was 17.3 % with benzaldehyde selectivity of 51.4 %. Oxidation of toluene has also been carried out in ionic liquid (bmimBr-$FeCl_3$) with H_2O_2 as the oxidant (Lu, et al., 2013). The reaction proceeded at 100 ^{o}C for 6 hours. Catalytic activity for this reaction showed 10.2 % conversion with 99 % selectivity to benzaldehyde and benzyl alcohol.

1.5.2 Oxidation of styrene

The oxidation of styrene leads to the formation of its oxide, aldehyde and ketone. Researchers often focus on the production of styrene oxide compared to benzaldehyde as the main product. Scheme 1.2 shows the formation of styrene oxide, benzaldehyde and acetophenon from styrene oxidation with H_2O_2 as the oxidant.



Scheme 1.2: Oxidation of styrene with H_2O_2 as oxidant and the resultant products

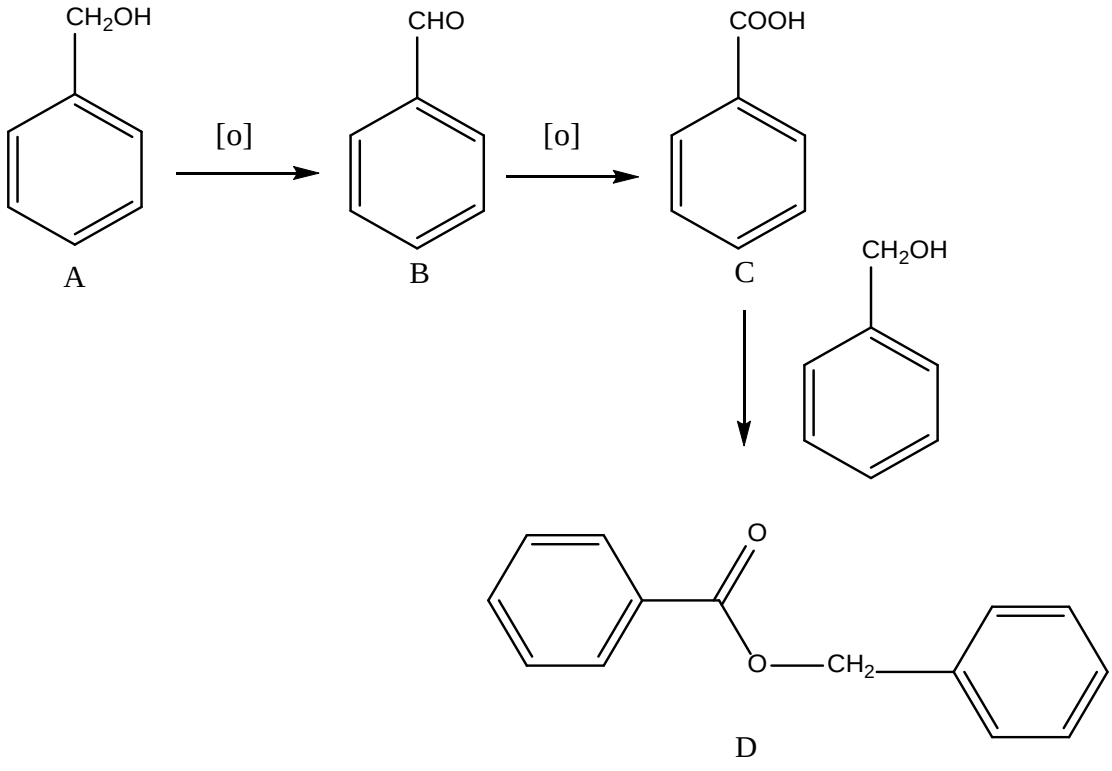
Research by Adam and Iqbal (2010, 2011) showed that silica incorporated with transition metals could be a catalyst for oxidation of styrene. In their research, chromium, molybdenum and tungsten have been incorporated into the silica. H_2O_2 was used as the oxidant. The highest styrene conversion was 99.92 % while the selectivity of benzaldehyde was 63.07 % when silica incorporated with chromium was used as the catalyst.

Mixed nano metal-oxide of Cu-Ni-Co was used as a catalyst for styrene oxidation (Valand, et al., 2013). The catalysts were synthesized with different metal loadings via ultrasonic cavitation-impregnation method. Acetonitrile and tert-butyl hydroperoxide (TBHP) were used as the solvent and oxidant respectively. The highest recorded styrene conversion using this catalyst was 73 % while the benzaldehyde selectivity was 72 %.

1.5.3 Oxidation of benzyl alcohol

Oxidation of alcohol to carbonyl compounds has been one of the most important organic chemistry for fine chemical industry. There are various catalytic reactions for benzyl alcohol oxidation. Oxidation of benzyl alcohol is a primary alcohol and the main product formed during oxidation is benzaldehyde. Various catalysts are used and different catalytic conditions will lead to different benzaldehyde selectivity.

The oxidation of benzyl alcohol will lead to the production of benzaldehyde and benzoic acid. As benzoic acid reacts with benzyl alcohol, benzyl benzoate will be produced. The general pathway for the transformation reactions of benzyl alcohol is shown in the scheme 1.3 below.



Scheme 1.3: The general reaction pathway for the reaction of benzyl alcohol: (A) benzyl alcohol to form (B) benzaldehyde, (C) benzoic acid and (D) benzyl benzoate

Aside from molecular oxygen, hydrogen peroxide is another green oxidant that can be use in the catalytic reaction. With a pH of 6.2, hydrogen peroxide has more active oxygen compared to molecular oxygen. It is also safe and easy to handle with water as the only by-product. In order to increase the hydrogen peroxide's oxidation capability, transition metal containing catalysts need to be applied so that the hydrogen peroxide can be activated.

Manganese doped ceria supported gold nanoparticles has been a catalyst for oxidation of benzyl alcohol (Mandal, et al., 2013). The catalyst was prepared via non-hydrothermal sol-gel method. The surface area of the catalyst is 29.34 m^2g^{-1} with a pore diameter of 13.0 nm. Molecular oxygen is used as the oxidant and the reaction was conducted at 90 ^oC for 3 hours. The benzaldehyde selectivity for this reaction is 99 % but the benzyl alcohol conversion was only 43.22 %. For the catalytic recyclability test, the benzyl alcohol conversion dropped to 24.87 %, which may be due to the growth of nanoparticles.

Copper has been employed in some catalysts in order to increase the catalytic activity such as copper(II) dimer-ligand, Cu-DAPyPTS-MCM-41 and MCM-41-CuPc. Mahmudov, et al., (2010) studied on the synthesis of a new copper(II) dimer with 3-(2-hydroxy-4-nitrophenylhydrazo)pentane-2,4-dione as a catalyst for the oxidation of cyclohexane and benzyl alcohol. In a 22-hour reaction, up to 99 % benzyl alcohol was converted with >99 % selectivity towards benzaldehyde. Although the conversion and selectivity of this reaction was high, but the 22 hours taken to carry out the reaction makes it less effective.

DAPyPTS-MCM-41 (N^4-(3-(triethoxysily)propyl)pyrimidine-2,4,6-triamine, a hybrid material, was synthesized via grafting method. TEOS was used as the source of silica to synthesize MCM-41 (Pérez, et al., 2012). Then, copper was

functionalized with the DAPyPTS-MCM-41 and acted as the catalyst for benzyl alcohol oxidation. The optimum benzyl alcohol conversion record was 58 % with 48 % selectivity of benzaldehyde.

On the other hand, Hamza and Srinivas (2009) studied on CuPc (copper phthalocyanine) complexes that were immobilized on Ti^{4+} and Al^{3+} containing MCM-41 as the support. After the metal was incorporated on MCM-41, the complexes were immobilized. During the optimization reaction of benzyl alcohol oxidation, dimethyl sulfoxide (DMSO) was selected as the best used solvent. More than 90 % conversion of benzyl alcohol was obtained when DMSO was used as the solvent. DMSO, a type of polar solvent, enhanced the catalytic activity by facilitating the formation of active oxygen species. Even though the prepared catalysts were heterogeneous, the TEOS used as a silica precursor is expensive. Thus, making the catalyst less desirable to be mass produced.

Metallic nanoparticles (MNP) have attracted great attention based on their potential as catalyst (Arellano, et al., 2011). Iron-based catalysts have been studied due to their environmentally benign, non-toxic and inexpensive metal. The catalytic action of Fe-NPs supported on various supports was studied in the oxidation of benzyl alcohol under microwave irradiation. One of the supports was MCM-41. Fe(NP)/MCM-41 acted as the catalyst for the oxidation of benzyl alcohol under the microwave irradiation. It produced benzaldehyde with selectivity of >95 %.

In other works, Adam and Ooi (2012) have synthesized metalloporphyrin ligand [tetrakis(*o*-chlorophenyl)porphyrinato]cobalt(II) complex where RHAC-NH_2 acted as the support. Rice husk ash (RHA), the source of silica, was used in the making of RHAC-NH_2. The catalyst, RHAC-CoPor, with the surface area of 114 m^2g^{-1} was tested in the oxidation of benzyl alcohol. RHAC-CoPor becomes one of

the best catalysts for benzyl alcohol oxidation, as the highest conversion of benzyl alcohol is 97.1 % with 97.7 % selectivity of benzaldehyde. There was only 2.3 % of benzoic acid as the by-product. The catalyst prepared was heterogeneous and resulted in high conversion and selectivity. There are some disadvantages as the catalyst and ligand preparation involved many processes and required more time. Thus, a simpler and better catalyst will be synthesized to overcome this problem.

1.6 Problem statements

Homogeneous catalyst is known as the best catalyst in catalytic study. However, their applications in catalytic reactions have some disadvantages. Homogeneous catalysts have difficulty in catalyst recovery and they are not environmentally friendly. Therefore, in order to overcome these problems various heterogeneous catalysts with microporous and mesoporous materials acting as the support have been synthesized.

Nowadays, tetraethoxysilane (TEOS), tetrapropoxysilane (TPOS) and tetramethoxysilane (TMSO) are used as the main silica source in synthesizing the support for catalysts. These commercial sources of silica are expensive and are toxic (Nakashima, et al, 1998).

Metal leaching problem is also frequently mentioned when metal acts as the catalyst for the oxidation reaction. The metal leaching can make the catalyst become deactivated only after the first usage. Thus, a solution must be made in order to prevent these catalysts from becoming homogeneous (Arends and Sheldon, 2001).

Benzaldehyde is an important material in the chemical industry. It has many uses and acts as an intermediate to form other new materials. Commercially, benzaldehyde formation has been carried out in the vapor phase and liquid phase and

is catalyzed by homogeneous catalysts such as cobalt catalyst. In order to increase the benzyl alcohol conversion and benzaldehyde selectivity, a new alternative heterogeneous catalyst needs to be produced to overcome all the above problems.

1.7 Objectives

Based on the problems listed in Section 1.6 above, the objectives of this study are:

1. To use silica form rice husk in order to synthesize MCM-41 incorporated with copper and iron respectively by sol-gel method (Cu-MCM-41 and Fe-MCM-41) with different metal loadings.
2. To characterize the Cu-MCM-41 and Fe-MCM-41 materials with fourier transform infrared spectroscopy (FT-IR), powder x-ray diffraction (XRD), nitrogen sorption analysis, transmission electron microscope (TEM), scanning electron microscopy-energy dispersive x-ray (SEM-EDX), UV-Vis diffuse reflectance spectroscopy (UV-Vis DR), atomic absorption spectroscopy (AAS) and pyridine test.
3. To investigate and optimize the catalytic performance of Cu-MCM-41 and Fe-MCM-41 for the oxidation of benzyl alcohol.

CHAPTER 2

METHODOLOGY

2.1 Raw Materials

The chemicals used in this study are shown in Table 2.1. All chemicals used were AR grade. The rice husk (RH) was obtained from Leong Guan Sdn. Bhd., Penang, Malaysia.

Table 2.1: Chemicals used in the catalyst preparation and catalytic reaction

Chemicals	**Purity**	**Brand**
Iron(III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$)	98.5 %	Qrec
Copper(II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$)	99.5 %	Qrec
Sodium hydroxide (NaOH)	99 %	Qrec
Nitric acid	65 %	Qrec
Hexadecyltrimethylammonium bromide (CTAB)	99 %	ACROS
Benzyl alcohol	97 %	Unilab
Hydrogen peroxide (H_2O_2)	30-32 %	Qrec
Dimethyl sulfoxide (DMSO)	99 %	Merck
Acetonitrile	99.5 %	Qrec

2.2 Extraction and modification of silica from rice husk (RH)

2.2.1 Preparations of Rice Husk Ash (RHA)

RH was washed with tap water and distilled water several times to remove dirt and other solid contaminants. Then it was dried at room temperature for 24 hours. The dried RH was stirred with 1.0 M nitric acid for 24 hours. The acid treated

RH was washed thoroughly with distilled water until the pH became constant (pH 5). The washed RH was dried at 100 ^{o}C before being calcined at 600 ^{o}C for 6 hours. The resulting RHA was white in color.

2.2.2 Preparations of iron-MCM-41 and copper-MCM-41

The Fe-MCM-41 and Cu-MCM-41 were prepared by sol-gel method. Firstly, 3.0 g of RHA was dissolved in 100 mL of 1.0 M sodium hydroxide (NaOH) followed by 2.9 g of CTAB and the solution was stirred until a clear solution was formed. Then, the sodium silicate solution was stirred for 24 hours at room temperature (RT). 1.141 g of $Cu(NO_3)_2.3H_2O$ (10 % (w/w)) and 2.170 g of $Fe(NO_3)_3.9H_2O$ **(**10 % (w/w)) was dissolved in 50 mL of 3.0 M nitric acid. The metal salt solution was titrated into the stirred sodium silicate solution until completion. The titration was continued with 3.0 M HNO_3 until the pH became 10. The titration was stopped and the gel produced was aged at RT for two days. After that, the gel was separated by centrifuge and dried at RT for 24 hours. The dried gel was calcined at 600 ^{o}C for 6 hours to remove the surfactant. The catalysts produced were labeled as Fe-10 for iron-MCM-41 and Cu-10 for copper-MCM-41.

2.2.3 Preparation of iron and copper supported on MCM-41

The incorporation of iron and copper with different loadings were done by following the same procedure as discussed in section 2.2.2 whereby the 10 % (w/w) of metal precursor was substituted with 5 %, 15 % and 20 % metal precursor. The catalysts obtained were labeled as Fe-5, Fe-15 and Fe-20 for the iron catalyst and Cu-5, Cu-15 and Cu-20 for the copper catalyst. Equation 2.1 shows the calculation of metal loading incorporated into the MCM-41.

$$\%\ of\ metal\ loading = \left(\frac{Mass\ of\ metal\ precursor\ x\ MW\ of\ metal}{MW\ of metal\ precursor\ x\ mass\ of\ MCM-41}\right) x\ 100 \qquad (2.1)$$

**MW: molecular weight*
Mass of MCM-41: 1.0 g

2.3 Characterization of the catalysts

2.3.1 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the catalysts were obtained using the FT-IR Spectrometer (Perkin Elmer System 2000) in the wave number range from 4000-400 cm^{-1}. The catalysts were dried at 100 ^{o}C for 24 hours to remove any adsorbed water molecules prior to the analysis before it was prepared with KBr disc for sample analysis. The FT-IR analysis was done at the FT-IR room, School of Chemical Sciences, Universiti Sains Malaysia.

2.3.2 Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Powder XRD was recorded using Siemens Diffractometer D5000, Kristalloflex diffractometer (voltage of 40 kV and current of 30 mA) diffractometer with Cu Kα (λ = 0.154 nm) radiation. For low angle diffraction pattern, scanning was performed from 1.5^{o} to 10^{o}. The analysis was performed at the Crystallography Laboratory, School of Physics, Universiti Sains Malaysia.

2.3.3 Nitrogen sorption analysis

Nitrogen sorption isotherms were measured using Micromeritic 2020 ASAP at the School of Chemical Sciences, Universiti Sains Malaysia. Degassing process was carried out at 150 ^{o}C under vacuum for 10 hours. The specific surface area was calculated using the BET model. For the pore size distribution's calculation, BJH model was used.

2.3.4 Transmission electron microscope (TEM)

Electron microscopy is a rather straightforward technique to determine the size and shape of supported particles. It can also reveal the information on the particle composition by detecting the x-rays that are produced by the interaction of the electrons with matter, or by analyzing how the electrons are diffracted. The TEM images were taken using a Philips CM12 Instrument with an analySIS Docu Version 3.2 image processing software. For the sample preparation, a small amount of the catalyst was suspended in 3 mL ethanol. After 5 minutes, one droplet of the suspension was dropped on a copper grid and allowed to stand for 2 minutes. Then, the droplet was dried using a small piece of filter paper. The TEM analysis was performed at the Electron Microscopy (EM) unit at the School of Biological Sciences, Universiti Sains Malaysia.

2.3.5 Scanning electron microscopy-energy dispersive X-ray (SEM-EDX)

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The focus beam of electrons interacts with electrons in the sample, producing various signals that contain information about the surface topography and composition of the sample. The SEM images and

EDX elemental analysis were analyzed using a Leo Supra 50 VP Field Emission Scanning Electron Microscope equipped with Oxford INCA 400 Energy Dispersive X-ray Microanalysis System. The catalyst was coated with platinum before being analyzed. The analysis was carried out at the Electron Microscopy (EM) unit at the School Biological Sciences, Universiti Sains Malaysia.

2.3.6 Atomic absorption spectroscopy (AAS)

The total amount of iron and copper present in MCM-41 silica matrix was determined by using Perkin Elmer AAnalyst 400. For the sample preparation, 0.05 g of catalyst was dissolved in 12 mL of freshly prepared aqua regia and 4 mL of hydrofluoric acid in a polytetrafluoroethylene bottle. The mixture was heated to 383 K before cooling to room temperature. As much as 10 mL of double deionized water together with 0.5 g of boric acid were added to the mixture. Then, the solution was quantitatively transferred into a 100 mL volumetric flask and was diluted to the mark with double deionized water. Acetylene/air fuel mixtures were used for the AAS flame detectors. The analysis was carried out in the MUPA laboratory, School of Chemical Sciences, Universiti Sains Malaysia.

2.3.7 Pyridine adsorption test

The copper-MCM-41 and iron-MCM-41 were tested for pyridine adsorption to detect Bronsted and Lewis acid sites present in the catalyst. Pyridine was used as an acidity probe in an in situ diffuse-reflectance FT-IR apparatus (NICOLET IR200 FT-IR). The catalyst was first made into a pellet. Then, it was placed in a desiccator equipped with a valve connected to a membrane vacuum pump. The catalyst sample was analyzed by FT-IR in six stages; before degassing (100 ^{o}C), after degassing and

followed by pyridine adsorption at 25 ^{o}C, 100 ^{o}C, 200 ^{o}C and 300 ^{o}C. The system runs for 60 min at each stage. The FT-IR spectra were recorded in the range of 1700 – 1400 cm^{-1}. The test was carried out at the FT-IR room, School of Chemical Sciences, Universiti Sains Malaysia

2.4 Catalytic Experiment

2.4.1 General reaction procedures

The liquid phase oxidation of benzyl alcohol was carried out in a two-necked 100 mL round bottom flask fitted with a reflux condenser. The catalyst was activated at 100 ^{o}C for 24 hours in order to remove any adsorb water molecules. The amount of benzyl alcohol and acetonitrile was fixed at 20 mmol and 10 mL, respectively. The round bottom flask was clamp with a retort stand and put in oil bath with temperature of 80 ^{o}C. Then, 0.05 g of the catalyst was added into the round bottom flask followed by 40 mmol of hydrogen peroxide. The reaction was carried out for 4 hours. 0.5 mL of aliquot was withdrawn and filtered at each hour by using a syringe. Before the samples were analyzed with GC and GC-MS, 1 µL of methanol was added as an internal standard.

Different metal loading in catalyst produce different catalysts (Fe-5, Fe-10, Fe-15, Fe-20, Cu-5, Cu-10, Cu-15, and Cu-20). Therefore, for each catalyst, the same catalytic reaction was conducted. Then, the catalytic reaction was optimized with different type of solvents, temperature, reaction time, molar ratio of benzyl alcohol and hydrogen peroxide and catalyst weight.

Leaching test was carried out after the optimization of the catalytic reaction. After 30 min, the catalyst was separated from the reaction mixture by directly applying to hot filtration process. Hot filtration process is a process where the

solution of the reaction was directly filtered to remove the catalyst after 30 minutes reaction started. Then, the filtrate obtained was returned to a clean, new flask maintained at the same conditions.

For the best catalyst identified in the oxidation of benzyl alcohol, recyclability test was studied. The used catalyst was washed with solvent and was dried at 100 ^{o}C for 24 hours. Then, the catalyst was reused back over three catalytic cycles.

2.5 Product Characterization

In order to monitor the catalytic activity of benzyl alcohol oxidation, a GC (Claurus 500, Perkin Elmer) equipped with a wax capillary column (30 m length and 0.25 mm inner diameter) and FID detector was used. The products were identified using GC-MS (Claurus 600, Perkin Elmer) equipped with the same column. For the GC and GC-MS analysis, 0.2 µL of the samples were injected and the condition used for separation and identification of the products is shown in Table 2.2. The conversion of benzyl alcohol and selectivity to benzaldehyde was calculated as shown in Appendix.

Table 2.2: Conditions of GC and GC-MS for separation and identification products of benzyl alcohol oxidation

Conditions	**GC**	**GC-MS**
Initial temperature	50 ^{o}C	50 ^{o}C
Ramp	15 ^{o}C min^{-1}	15 ^{o}C min^{-1}
Final temperature	230 ^{o}C	230 ^{o}C
Injector temperature	240 ^{o}C	240 ^{o}C
Total time	12.67	12.67
Carrier	N_2	He